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Title: Preparation, Electromechanical, and Structural Study of Carbon Nanotube/Gelatin Nanocomposites

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14. ABSTRACT

Multi-walled carbon nanotube (MWNT)/gelatin composites by dispersion of MWNT through ultrasonication in an aqueous medium with anionic surfactant sodium dodecyl sulfate (SDS). The swelling behavior and the bending mechanism of the composite and pure gelatin films were studied in order to clarify the potential use of MWNT in the gelatin actuator. The response of the composite and pure hydrogel to the applied electrical field in the NaCl aqueous solution was investigated. Both of the composite and pure hydrogel showed a two-stage bending phenomenon, an early bending towards the anode and a later bending to towards the cathode. An investigation of the mechanism of this bending phenomenon was performed based on osmotic pressure difference at the inter-phase between the hydrogel film and salt solution. The swelling behavior of the composite was studied by immersion of the vacuum-dried gels samples into a 0.1 M NaCl aqueous solution at room temperature. The incorporation of MWNT gradually decreased the swelling of the hydrogel and exerted no effect on the swelling mechanism which followed the second order kinetic. Both the bound and unbound water contents (measured from DSC) decreased with the addition of MWNT. This phenomenon might be due to the hydrophobic effect of the MWNT and increase in crosslinking density by increasing the MWNT concentration.

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Final Report on

Preparation, Electromechanical and Structural Study of

Carbon Nanotube/Gelatin Nanocomposite

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Abstract: We prepared multi-walled carbon nanotube (MWNT)/gelatin composites by dispersion of MWNT through ultrasonication in an aqueous medium with anionic surfactant sodium dodecyl sulfate (SDS). The swelling behavior and the bending mechanism of the composite and pure gelatin films were studied in order to clarify the potential use of MWNT in the gelatin actuator. The response of the composite and pure hydrogel to the applied electrical field in the NaCl aqueous solution was investigated. Both of the composite and pure hydrogel showed a two-stage bending phenomenon, an early bending towards the anode and a later bending to towards the cathode. We investigated the mechanism of this bending phenomenon based on osmotic pressure difference at the inter-phase between the hydrogel film and salt solution. The swelling behavior of the composite was studied by immersion of the vacuum-dried gels samples into a 0.1 M NaCl aqueous solution at room temperature. The incorporation of MWNT gradually decreased the swelling of the hydrogel and exerted no effect on the swelling mechanism which followed the second order kinetic. Both the bound and unbound water contents (measured from DSC) decreased with the addition of MWNT. This phenomenon might be due to the hydrophobic effect of the MWNT and increase in crosslinking density by increasing the MWNT concentration**.**

Introduction

Soft engineered actuation systems that have properties more in common with biological than traditional engineering materials have recently attracted much attention. Hydrogel is one material that can be used for the development of such actuation systems, as it undergoes reversible transformation, which results in dramatic swelling and shrinking upon exposure and removal of stimuli [1] such as temperature [2-4], pH [5], solvent composition, ionic strength [6-7],and magnetic and electric fields [8-9]. Among these possibilities, an electric stimulus seems to be particularly interesting [10-11] in view of the fact that electric field is the most conventional and convenient stimulus from the point of signal control [12]. Bending deformation (or dimensional (volume) changes) of the polyelectrolytic hydrogels by electric field [13-14] may find application as an "artificial" muscle, and will be of great importance for robotic e.g switches [15], electromechanical engines [16], chemical valves [17], and controlled drug delivery [18]. The main requirements of such devices are low maintenance voltage, light weight, large displacements, high force, fast response, and long life cycle. Many research activities are focused on hydrogels which are sensitively responsive to electric stimuli. Kim et al studied the response of an alginate/poly (diallyldimethylammoniumchloride) interpenetrating network (IPN) hydrogel to an electric field in an HCl solution [19]. Schreyer et al studied polyacrylonitrile gel fibers [20], Sun et al reported chitosan/poly (ethylene glycol) [21], and Daunert et al also investigated acrylic acid/acrylamide reinforced with a conductive polypyrrole/carbon black composite [22].

Gelatin is a high molecular weight polypeptide obtained by controlled hydrolysis of collagen [23]. It is a good film and particle forming material [24] with uses in

medicine such as plasma expander, wound dressing, adhesive, and controlled drug delivery. The most interesting feature of gelatin is that it can be used for the production of practical biocompatible materials [25-26]. However, gelatin has limitations in practical applications owing to its weak mechanical strength and degradation in vivo [27]. In order to use this material in practical applications, the structure needs to be reinforced either through crosslinking or some filler materials. However the presence of residual crosslinking agents can lead to toxic side effects [28]. Hence, a material that may aid not only to structural stability but also to mechanical strength is needed. Carbon nanotubes (CNTs) are a new form of carbon, consisting of concentric cylinders of graphite layers rolled into graphene cylinders. The combination of their shape with the ability to undergo large deformations [29-32] without damage may find their use in polymer systems. [33]. They have high strength, high surface area (creating a large interfacial region, which can have properties different from bulk material), and the ability to buckle like rubber in a reversible manner. Their excellent electrical properties also make them attractive candidates for new materials [34-36]. They also have shown great promise as possible reinforcing filler in composites from previous research regarding mechanical properties [37-38]. The potential biological applications of single-walled and multi-walled carbon nanotubes (SWNT and MWNT) have recently attracted much attention [39], and include helical crystallization of protein [40], immobilization of biological species on both SWNT and MWNT as a potential biosensor [41], and bioelectronic nanomaterial [42].

In the present study, we used MWNT as a reinforcing material in gelatin which was dispersed with ionic surfactant (i.e. SDS) in an aqueous medium. The swelling and

electro responsive behaviour of the pure and MWNT/ gelatin composite hydrogels were studied.

Materials and methods

Materials

Gelatin (Type B, bovine skin) and NaCl (reagent grade, purity 99%) were purchased from sigma Aldrich. Sodium dodecyl sulfate (SDS) was purchased from DC Chemical©, Republic of Korea. MWNTs (CVD, MWNT–95) were supplied by ILJIN Nanotech© and were manufactured by thermal chemical vapor deposition. The diameter and length of the studied MWNT were 10-20 nm and 10-50 μm respectively and its purity was higher then 97wt% [43].

Preparation of the composite

MWNTs were dispersed by ultrasonicator (Microprocessor controlled-2004) in an aqueous medium with SDS. Gelatin was dissolved in deionized water above 40 $^\circ$C in a water bath. The two solutions were mixed, ultrasonicated again, and poured onto glass petri dish for film casting. Excess surfactant (sodium dodecyl sulfate) was removed from the films by soaking in deionized water for 24 hours with regular replacement of the water. Finally, the films were dried in a vacuum oven at 60 $^\circ$C and then removed from the Petri dish.

Swelling study

The prepared samples were thoroughly dried under vacuum at 60 ^{o}C until constant weight before swelling. Rectangular samples of the dimension (16 [length] × 15 [wide] × and 1.2 [thick] mm^3) were used for swelling. Each sample was immersed in a vial containing 10 mL of the 0.1 M NaCl aqueous solution. The samples were kept at room temperature for the duration of swelling experiments. Each sample was taken out of the vial at regular intervals, wiped between filter papers to remove the excess surface water and weighed. The swelling ratio was calculated using the following equation 1;

$$Swelling\ ratio\ (\%) = \frac{(W_o - W)}{W} \times 100 \text{---------(1)}$$

where W_o is the weight of the swollen sample and W is the weight of the dried sample.

Measurement of bound and free water

The states of water (bound [nonfreezing] and unbound [freezing and freeze bound]) waters in the hydrogel samples were determined by differential scanning calorimetry (DSC) using Dupont 2000 Thermal analyzer at a heating rate of 5 ^{o}C/min with nitrogen flow. Each sample was immersed in a vial containing 10 mL of the deionized water and allowed to swell to equilibrium time. The sealed pan was quickly frozen to -40 ^{o}C and then allowed to come to equilibrium for several minutes. The sample was then heated at a scanning speed of 5 ^{o}C/min with nitrogen flow. The sample pan was removed from the DSC and dried at 105 ^{o}C. The total amount of water was calculated by subtracting the weight of the sample pan and dried sample pan. The amounts of unbound and bounded waters were calculated from the melting enthalpies using the equation below. This equation assumes that the heat of fusion of free water in the hydrogel (Q_{endo}) is the same as that of ice (Q_f 79.9cal/g).

$$W_b(\%) = W_t - (W_f + W_{fb}) = W_t - (\frac{Q_{endo}}{Q_f}) \times 100 \text{----}(2)$$

where $W_t(\%)$ is the total water, $W_b(\%)$ is the amount of bound water, W_f and W_{fb} are the amounts of free water and freezing bound water; Q_{endo} and Q_f are the heat of fusion of free water and ice, respectively.

Morphology

Scanning electron microscopy (SEM) of the non-freezed vacuum dried and freeze-dried gels was performed using a Hitachi 570. The specimens with the dimensions of 16 [length] × 15 [wide] × 1.2 [thick] mm³ were used for freeze drying. The specimens were swelled to equilibrium in deionized water and blotted with filter paper to remove the surface water. The swelled specimens were then frozen in the freezer (IISHIN DF9007) at -70 °C for 30 minutes and dried in the drying chamber (IISHIN FD5505) in the frozen state at -54 °C for 16 hours. The non-freezed and vacuum-dried samples were fractured in liquid nitrogen. Samples were fixed on the brass holder and coated with platinum prior to SEM observation.

Electrochemical characterization

The electrochemical behavior of MWNT/gelatin composite films was studied under the DC electric field. A 0.1 M NaCl aqueous solution was poured into a glass beaker with two parallel platinum electrodes (50 [length] × 10 [wide] × 3 [thick] mm³), which were 52 mm apart. The dimensions of the samples were 30 [length] × 4[wide] × 2[thick] mm³. DC voltage was applied to the solution across the electrodes. One end of the sample was fixed (cantilever type) during the bending test. The deformation was recorded with a

digital camera at a fixed position and fixed focus, and the deflection was expressed as x and y ratio where x and y are the positions of the free end of the film on x-y coordinate [44], as shown in Figure 8.

Results and discussion

Swelling Behaviour

Figure 1 shows the swelling of 0.8 wt% MWNT/gelatin composite which increased up to 0.2 M concentration of NaCl in an aqueous solution and then decreased with further increase in the concentration. The increase in the charge density on the polyampholytic hydrogel network at low or moderate concentrations of NaCl (low ionic strength media) might increase the swelling ratio of composite. However, further increase of the concentration of the NaCl caused decrease in swelling of the composite, owing to the formation of the ion pairs between the network charges and the counter ions. Ion pairs strongly influenced the conformation of polyelectrolytic chains in hydrogel [45], which might have resulted in the additional crosslinking of the network, as a result of the aggregation of ion pairs into multiples by dipole–dipole interaction [46].
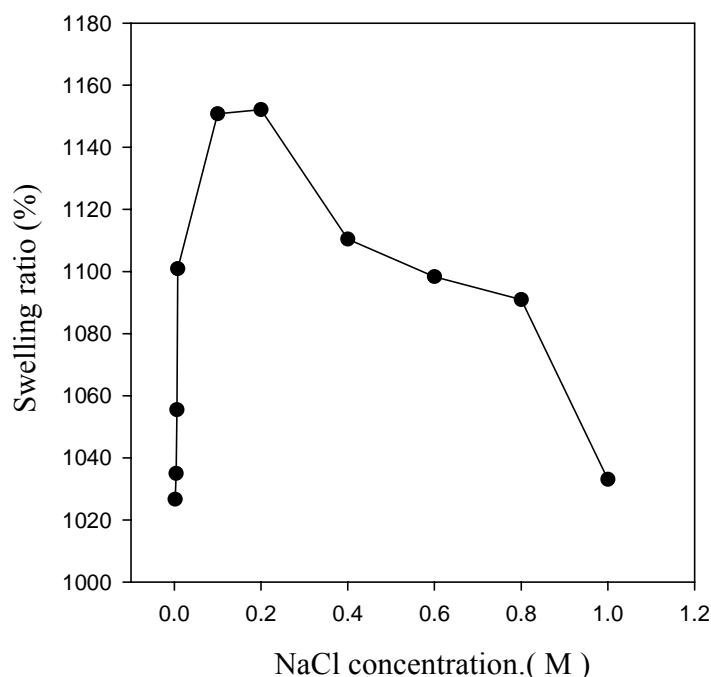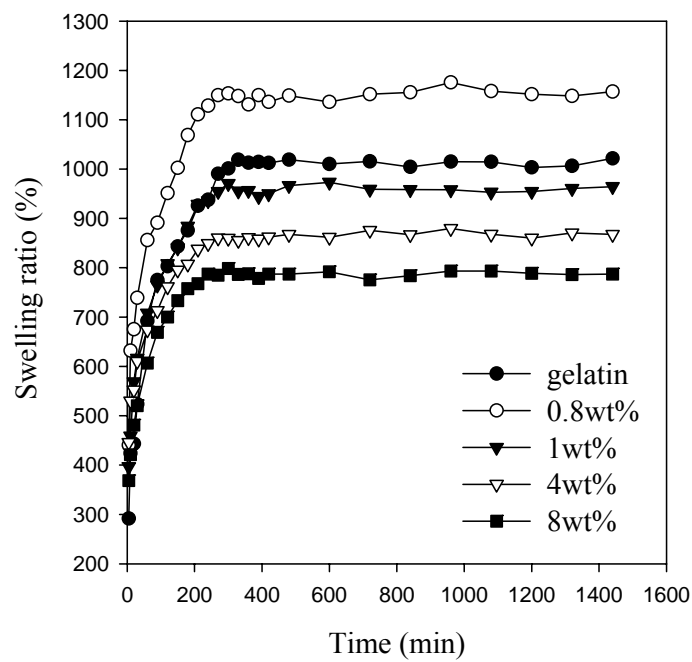
Figure 1. Swelling of the 0.8wt% MWNT/gelatin composite as a function of NaCl concentration

Figure 2 illustrates the swelling kinetic curves of gelatin and of MWNT/gelatin composites as a function of the MWNT concentration in a 0.1 M aqueous NaCl solution. Swelling of gelatin and composites became constant around four hours. Swelling increased in case of 0.8 wt% and then decreased with further addition of the MWNT to gelatin. This might be due to the slight hydrophilic nature of the MWNT/gelatin composite due to the possible interaction of the negative sulphonic (- SO_3^-) group of the surfactant on the MWNT and the positive ammonium (-NH_3^+) group of the polyampholytic polymer [47-48]. The hydrophobic chain of the surfactant can essentially interact with the side walls of the nanotubes though hydrophobic interaction and thereby anchors the surfactant molecules onto the surface of MWNT, leaving the hydrophilic head groups to interact with the polymer. The binding of the positive group of the

polymer with the hydrated end group of the surfactant has also been reported [49]. This might result in relatively more negative carboxylic groups than the positive ammonium groups in the polyampholytic polymer, which might be responsible for the hydrophilic nature of the polymer composite hydrogel. However, further increase in MWNT caused decrease swelling which is possibly due to increased hydrophobicity as result of the relative decrease in the SDS concentration on the MWNT and enhanced crosslinking density as result of the increase in the crosslinking sites. Hydrophobicity is known to cause relative aggregation of the MWNT which reduces diffusion of water through the MWNT net work [28].
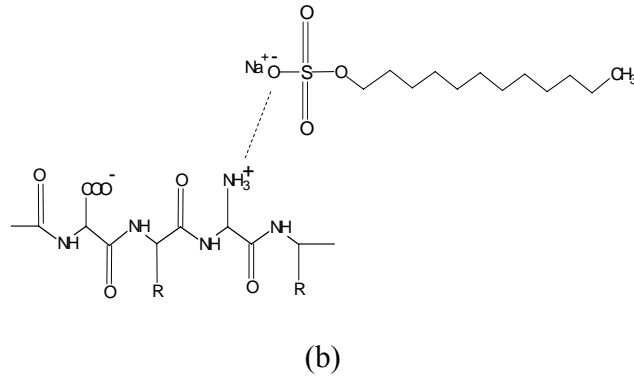

(a)

(b)

Figure 2. Swelling curves of the gelatin and MWNT/gelatin composite. (b) Scheme for the possible interaction of the gelatin and sodium dodceyl sulfate (SDS).

The kinetics of gelatin can be described by the following second order rate equation [50].

$$\frac{dW}{dt} = k(W_\infty - W)^2 \quad \text{……………..} \quad (3)$$

where k is the rate constant, W_∞ represents the maximum or equilibrium solvent uptake, W is the solvent absorbed per gram of gelatin at time t, and $(W_\infty - W)$ is the swelling capacity. It can be written by integrating and rearranging equation 3 as follows

$$\frac{t}{W} = A + Bt \quad \text{………………………} \quad (4)$$

where A and B are the intercept and slope of the plots of t/W verses time (t) respectively (i.e., $A = 1/K_\infty^2$ and $B = 1/W_\infty$). The swelling data presented in Figure 2 is calculated according to equation 4. Figure 3 shows linear regressions of the plot of t/W verses t. The straight lines indicate that both gelatin and MWNT/gelatin composite follow second order kinetic and the swelling mechanism of gelatin is not affected by the addition of MWNT. The constants A and B as well as the corresponding values of W_∞ and K_∞,

were obtained from the intercept and slope of linear regression curves as listed in Table 1. W_∞ and K_∞ of the MWNT/gelatin composite decrease with increase in the concentration of MWNT.
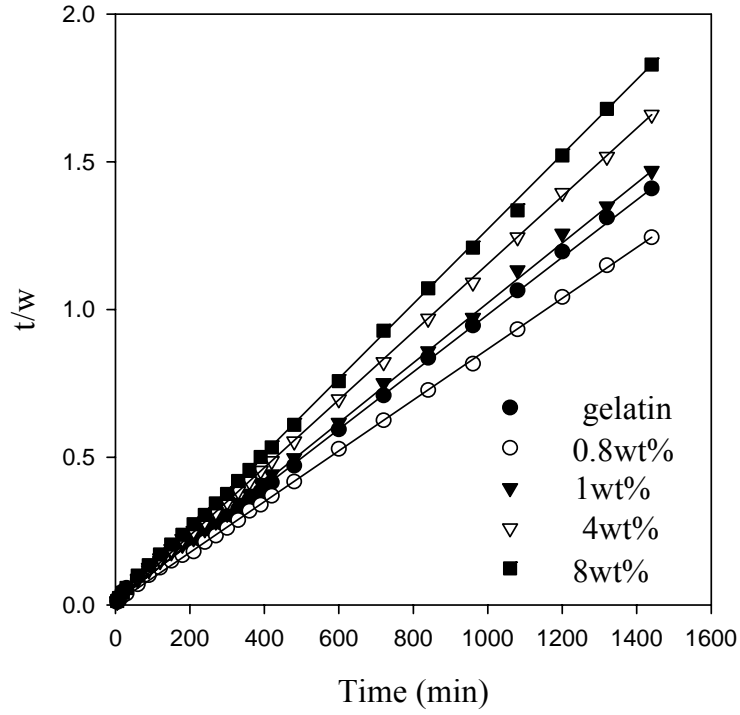

Figure 3. Linear regression of the swelling curves of Figure 2 according to equation (2).

Table 1. K_∞ and W_∞ of gelatin and the MWNT/gelatin composites at various concentrations (wt %) of the MWNT.

Sample	A	B	W_∞	K_∞
Gelatin	0.01919	9.68258×10^{-4}	1033	7.067
0.8wt%	0.0105	8.55269×10^{-4}	1170	9.759

1wt%	0.01567	0.00101	990	7.988
4wt%	0.0117	0.114	877	9.245
8wt%	0.01218	0.00125	800	9.061

Determination of Bound Water and unbound water in the Composite

There have been a number of various studies concerning the states of water in polymers [51]. There are three types of waters in hydrogel [52]: freezing, freeze bound (intermediate water), nonfreezing water. Free [freezing and freeze bound] water shows a melting endotherm, does not form hydrogen bonds with the polymer molecules, and shows greater degree of mobility. Bound [nonfreezing] water refers to water molecules that are hydrogen-bonded to the polymer chain, and shows no melting peak and little mobility. Freeze bound interact with the polymer molecules and has a melting endotherm slightly below 0 ^{o}C. Free water (freezing and freezing bound water) is calculated by the ratio of the endothermic peak of the swollen hydrogel to the endothermic peak of the heat of fusion of the pure water. Bound water is calculated as a difference between total water and free water. Table 2 and Figure 4 show bound (nonfreezing) water and the free (freezing and freeze bound) water. Total, bound and free waters increased for 0.8 wt% MWNT/gelatin composite hydrogel and then decreased with further addition of the MWNT content. The increased crosslinking and hydrophobic effect of the MWNTmight have resulted in the decreased hydrogen bonding of water with polymer matrix and the condensed structure as confirmed by SEM micrographs as shown in Figure 6 (will be discussed later).
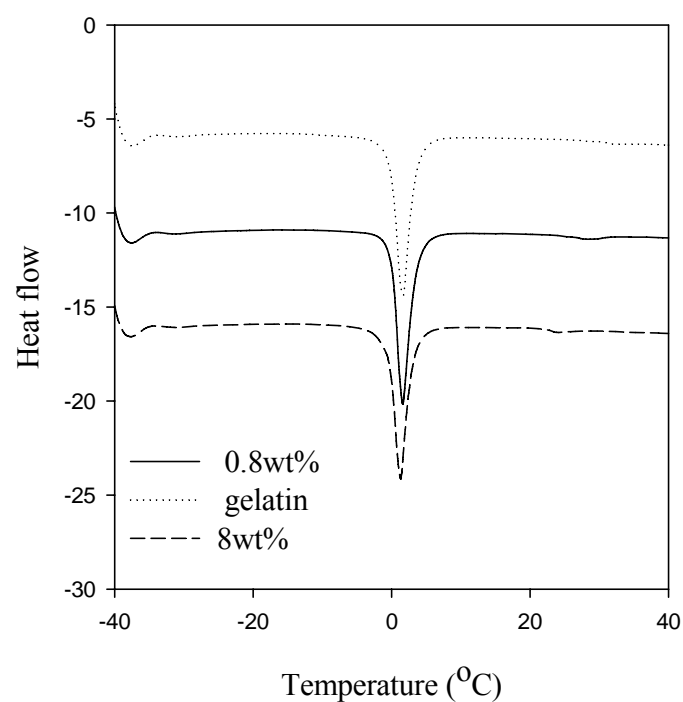
Figure 4. DSC thermogarms of fully swollen hydrogels of gelatin and MWNT/gelatin composites.

Table 2**.** States of water in gelatin and MWNT/gelatin composite hydrogels calculated by DSC analysis.

Sample	Scanning rate	Enthalpy (J/g)	Total water (%)	Bound water (%)	Free water (%)
Gelatin	5 ^{o}C/min with nitrogen flow	271.4	82.89	1.99	80.90
0.8wt%	5 ^{o}C /min with nitrogen flow	284.8	88.81	3.91	84.9

| 8wt% | 5 °C /min with nitrogen flow | 233.7 | 72.22 | 2.79 | 69.43 |

Morphology

Figure 5 visualizes the SEM micrographs of the fractured surfaces of the MWNT/gelatin composites films. MWNT showed good dispersion in the polymer matrix at low concentrations with the aid of surfactant whereas the dispersion was relatively poor at high concentrations. MWNTs are difficult to handle to form the homogeneous MWNT/polymer film by solution evaporation, due to the poor dispersion as result of van der waal attractive forces between the individual MWNTs. In order to obtain homogeneous dispersion of MWNT in the polymer matrix, MWNT can be dispersed in the aqueous medium through non-covalent functionlization of MWNT with a supramolecular surfactant (e.g., SDS), as demonstrated elsewhere [53]. The hydrophobic chain of the surfactant can essentially interact with the side walls of the nanotubes though hydrophobic interaction and thereby anchors the surfactant molecules onto the surface of MWNT, leaving the hydrophilic head groups to interact with solution. The hydrophilic head groups of the surfactant molecules created negative charge distribution between MWNT which might result in MWNT to stay well separated. However, further increase in MWNT leads to relatively poor dispersion in the polymer matrix due to increased hydrophobic surfaces as result of the decrease in the concentration of SDS molecules on the MWNT surface.
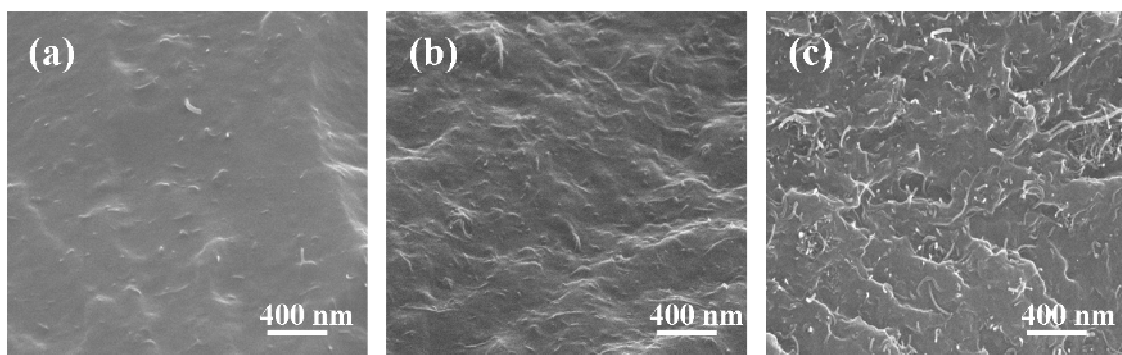
Figure 5. SEM micrographs of (a) 1 wt%, (b) 4 wt% and 8 wt% samples fractured in liquid nitrogen and imaged from the fractured section.

Figure 6 shows the morphology of freeze-dried samples of MWNT/gelatin composites and gelatin films. Figure 6a to 6d represent the surface morphology and Figure 6e to 6h shows the fractured surface. An almost closed with skin sheathing and porous surfaces were observed for the MWNT composite (1 wt%, 4 wt%, and 8 wt %) and gelatin, respectively. The internal micro structure from the fractured surface showed a layered condensed structure with very little pore structure for 4 and 8 wt% although almost open structure was observed for gelatin. The condensed structures in case of 4 and 8 wt% samples are possibly attributable to the increased interactions between MWNT and the polymer matrix as a result of the increased crosslinking sites.
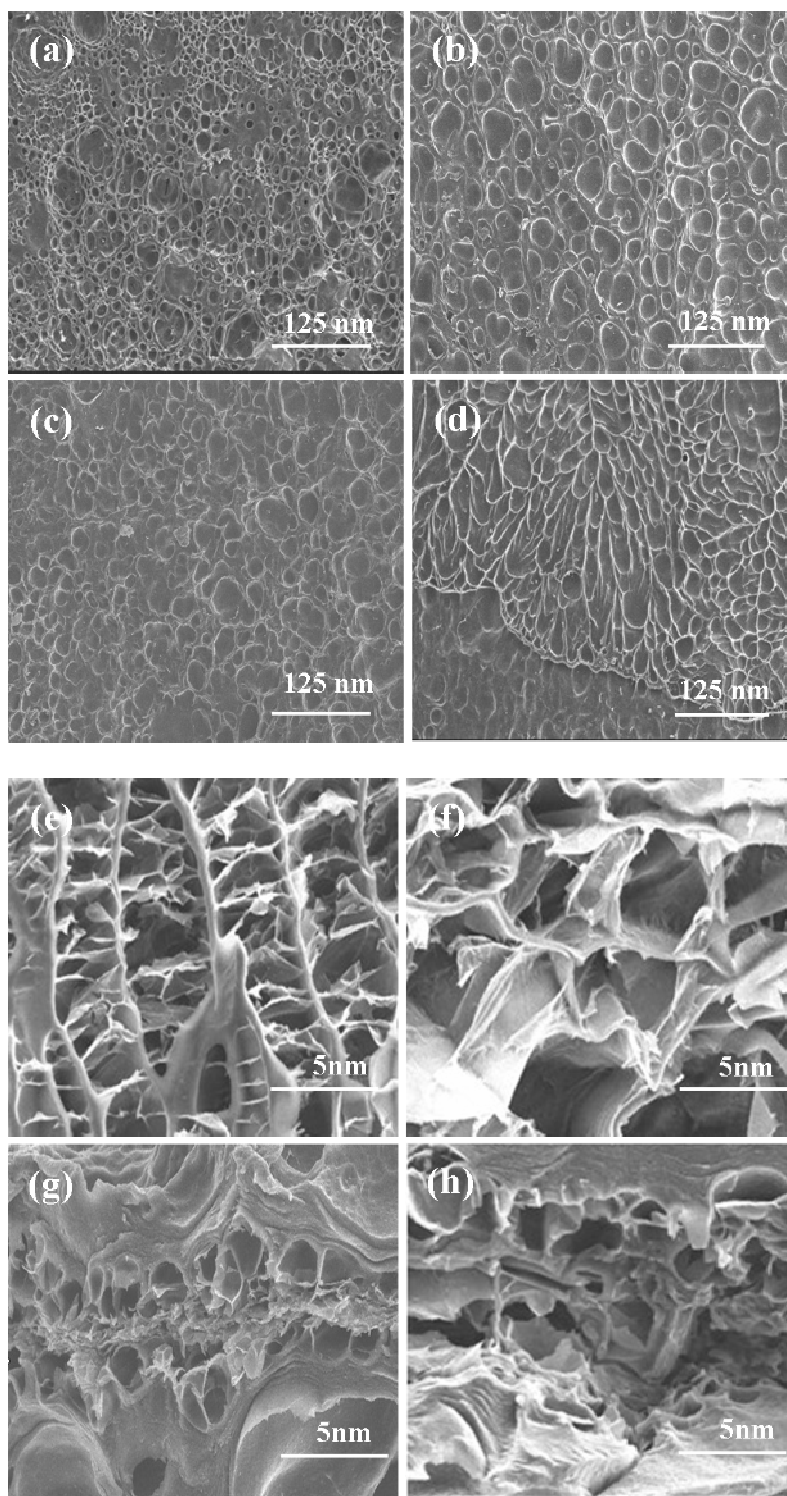
Figure 6. SEM micrographs of the samples swelled to equilibrium, freezed at −70 °C, and dried at − 45 °C, (a) gelatin, (b) 1 wt% (c) 4 wt% and (d) 8 wt% imaged from the Surface, and (e) gelatin, (f) 1 wt% (g) 4 wt% and (h) 8 wt% imaged from the fractured surface.

Figure 7a shows the proposed scheme for incorporation of MWNT into the gelatin fibrils. The left side shows the solubilization of gelatin and dispersion of the MWNT in aqueous SDS solution. The right side shows the incorporation of the MWNT into the gelatin fibrils and a possible cross-linked MWNT /gelatin composite. The interaction between CNT and SDS [53] and between the surfactant and prtotenious material has been reported [49, 54]. Figure 7b illustrates the stability of the MWNT/gelatin composites. All the MWNT/gelatin composites have shown good stability compared to gelatin. The increase in the MWNT content possibly leads to increased stability of gelatin which might be attributed to the hydrophobic nature of MWNT as well as the increased crosslinking density.
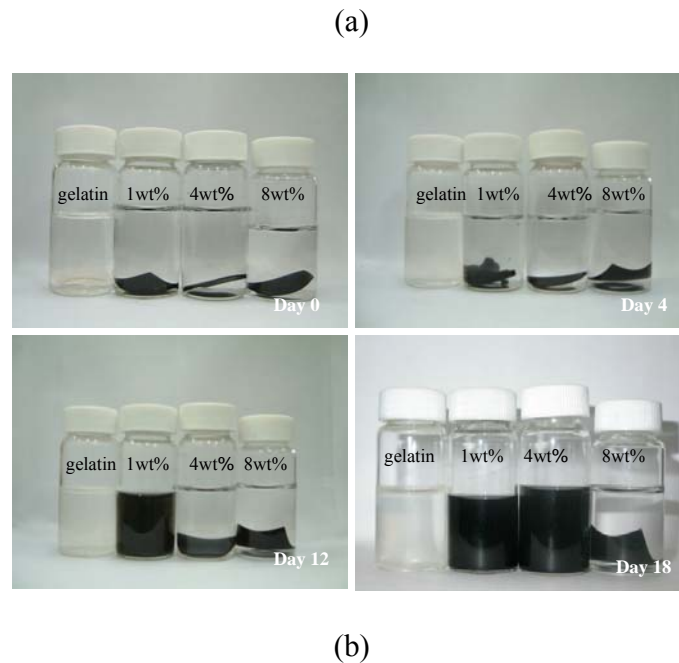
Solubilized gelatin

MWNTs dispersed in surfactant

MWNTs incorporated in gelatin

18

(a)

(b)
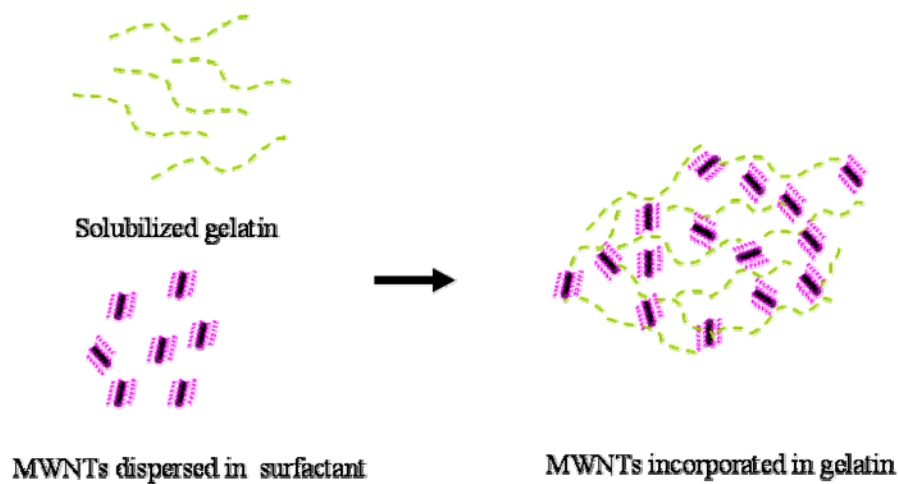
Figure 7. (a) Schematic of the incorporation of MWNT gelatin and possible crosslinking (b) Stability study of the MWNT/gelatin composites in 0.1 M aqueous NaCl solution at room temperature.

Bending characterization

The electro-responsive behavior in polyelectrolyte hydrogel was explained by various phenomena. However, the phenomenon is not well understood yet despite numerous hypotheses concerning the mechanism involved in the electro-actuation. Earlier researchers have described the bending of gel by osmotic pressure difference between the anode and cathode sides of the gel. These are considered to be the most accepted hypotheses to explain electro actuation of the hydrogel to date [55-56]. The proposed system is a non-contacting cantilever type with one end fixed. The gel strip and the electrodes are far apart from each other in the experimental cell as shown in Figure 8.
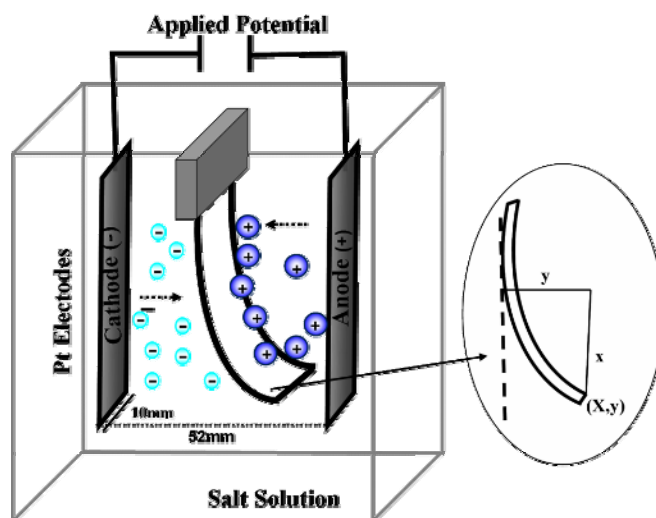
Figure 8. Experimental set up for the electro chemical characterization of the hydrogel.

Figure 9 depicts the electrochemical phenomenon of MWNT/gelatin composite hydrogel. The hydrogels show a two-stage bending under the applied DC current. The initial movement of the hydrogel was towards the anode and the later one towards the cathode. The initial bending towards the anode might occur due to the accumulation of the positive ions on the anode-side film surface. The accumulated ions created osmotic pressure difference at the anode side. The osmotic pressure difference causes more water to penetrate into gel at the cathode side than the anode side leading the gel to bend towards the anode as shown in Figure 9c. The accumulated positive ions (counter ions) were diffused into the gel after some time as shown in Figure 9d. This might decrease the anode-side positive ionic concentration inside gel film by the movement of the positive ions to the cathode, leading to osmotic pressure difference at the cathode side which causes the swelling of the gel film at the anode side. This in turn would cause the bending towards the cathode [45].
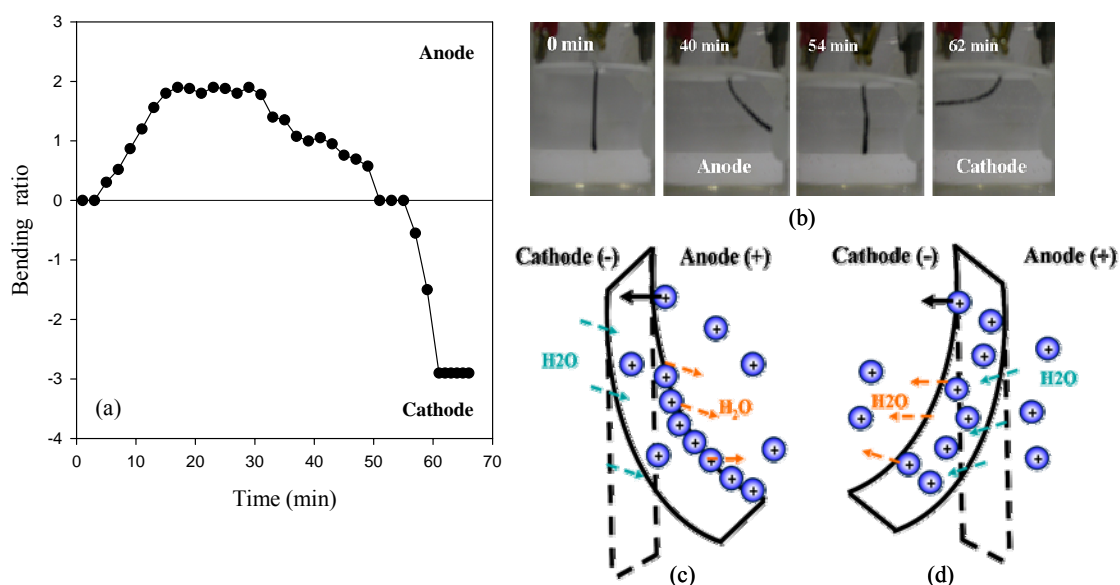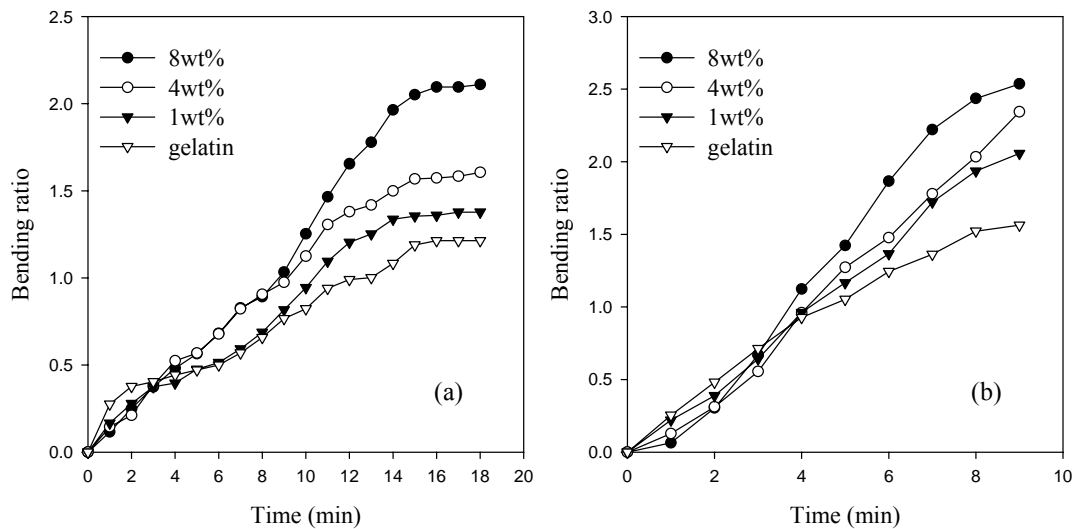
Figure 9. Bending behaviour of the gelatin and MWNT/gelatin composite hydrogels of dimension (30 [length] × 4[wide] × 2[thick] mm^3) in 0.1 M NaCl aqueous solution at applied potential of 6 volts (a) Bending curve of the MWNT/gelatin composite, (b) representative digital camera images of the bending phenomenon, and (c and d) cartoonic illustration of the proposed mechanism for the reported behaviour.

Figure 10 shows bending of gelatin and MWNT/gelatin composites in a 0.1 M NaCl aqueous solution using DC current. Figure 10a and 10b show the initial dry state bending at 6 and 9 volts respectively, and Figure 10c and 10d show the wet state bending (swelled above its equilibrium swelling time before bending in 0.1 M NaCl aqueous solution) at 6 and 9 volts respectively. The initial rate of bending of 1, 4, and 8 wt% at 6 volts was slow compared to gelatin which can be attributed to the initial stiffness of 1, 4, and 8 wt% MWNT/gelatin composites. All three samples showed large bending after the

initial slow deformation, which might be due to the gradual accumulation of the large number of positive ions (counter ions) at the anode-side interface leading to large bending. Gelatin and 1wt% samples reached to equilibrium rapidly with no further bending due to the quick diffusion of positive ions into the gel which might reduce the osmotic pressure gradient at the anode side. The same effect was found at high voltage (9volts) as shown in Figure 10 b where the quick accumulation of counter ions at the interface on the anode side might lead to an increased rate and large bending of the gel. Figure 10c shows the bending of the wet state samples at 6 volts, the same initial behaviour can be seen as was observed for the dry state sample. However, equilibrium was achieved in case of wet state, which can be attributed to the decrease in osmotic pressure at the anode and increase at the cathode, as result of the moment of positive ions towards the cathode. In case of 9 volts as shown in Figure 10d, increased rate of bending could be observed which might be attributed to the same effect as in the dry state.
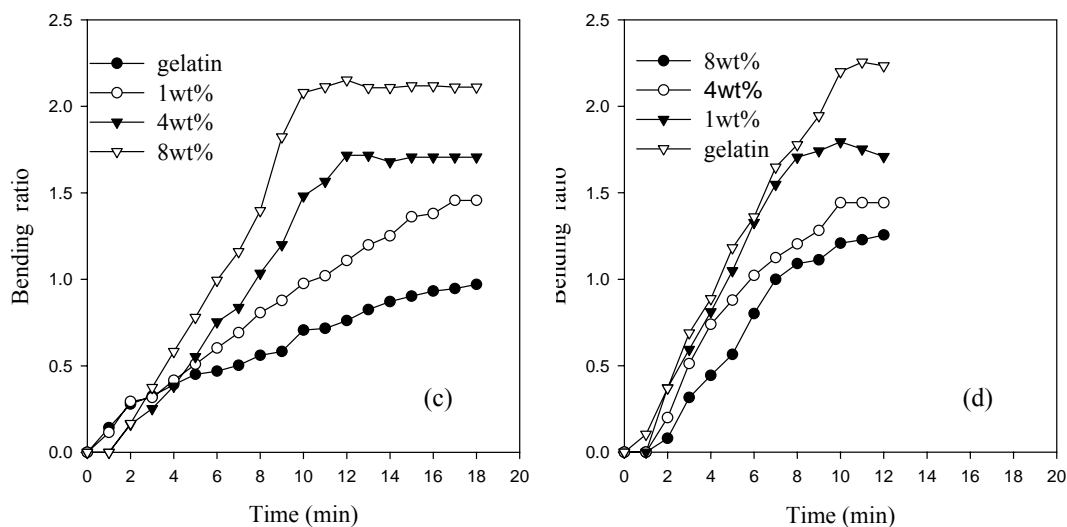
Figure 10. Time courses for bending of gelatin and MWNT/gelatin composite hydrogels of dimension (30 [length] × 4[wide] × 2[thick] mm^3) in 0.1a M NaCl aqueous solution towards the anode at applied potential, (a) dry state at 6 volts (b) dry state at 9 volts, (c) wet state at 6 volts, and (d) wet state at 9 volts.

Figure 11 shows the later stage step wise on and off bending behavior (when the gel film started bending towards the cathode. The DC current was switch off and the gel film was allow come to zero) of gelatin and the composite hydrogels. Not much difference can be observed in the initial bending for the samples. However, 8 wt% MWNT/gelatin showed more bending compared to gelatin as the time goes on, which can be due to the condensed structure, resulting in stability and large bending strain of MWNT. Whereas the low bending in case of gelatin may due to the quick degradation of the gel film caused by the electric stimuli which may erode the film to a great extent on exposure to DC current for longer time.
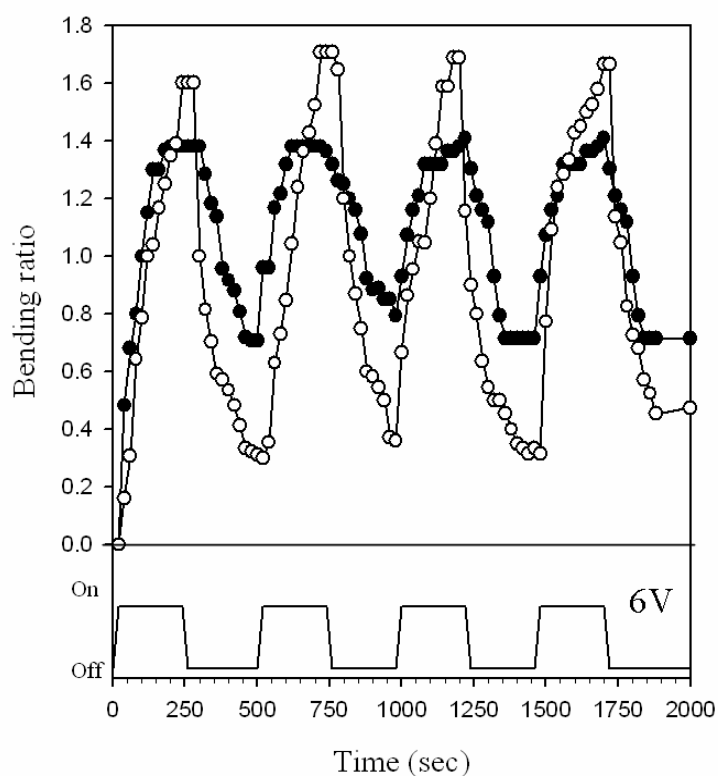
Figure 11**.** On and off bending behaviour of MWNT/gelatin composite hydrogels of dimension (30 [length] × 4[wide] × 2[thick] mm^3) in 0.1 M NaCl aqueous solution to wards the cathode at an applied voltage of 6 volts.

4. Conclusions

MWNT/ gelatin composites were prepared by dispersing MWNT in an aqueous medium *via* surfactant. The swelling, electromechanical behaviour and the morphology were studied. The composite showed decreased swelling with addition of the MWNT, which showed that MWNT inhibits swelling. MWNT may inhibit swelling not only by hydrophobic interaction but also by aiding in crosslinking via polymer/surfactant

interaction. Decrease in the swelling also decreases the degradability of the composite which show that MWNT maintain the stability of the composite. The bending mechanism can be explained on the osmotic pressure difference at the solution gel interface. Bending toward the anode at the first stage is attributed to the accumulation of the positive ions at the anode side of the gel film in the solution. The accumulated ions created osmotic pressure difference at the anode side. The osmotic pressure difference causes more water to penetrate into gel at the cathode side than the anode side leading the gel to bend towards the anode. The later bending towards the cathode may attribute to the diffusion of the positive ions into the gel which creates an osmotic pressure difference on the cathode side of the gel. The composite showed good reversible behaviour compared to the gelatin which might be due to the condensed structure of the composite compared to the gelatin, which erodes to a great extent on exposure to DC current for longer time.

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